

# Thermoplasticization of Bagasse. II. Dimensional Stability and Mechanical Properties of Esterified Bagasse Composite

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**ABSTRACT:** This research was to investigate the conversion of bagasse into a thermomoldable material through esterification of the fiber matrix. For this purpose, bagasse fiber was esterified in the absence of solvent using succinic anhydride. The dimensional stability and mechanical properties of composites prepared from the esterified fibers were studied. Dimensional stability was found to be dependent on the total ester and monoester/diester content of esterified fibers and increased with increasing total ester and monoester content of the fibers. The mechanical properties (bending strength, tensile strength, and hardness) were enhanced with increasing monoester contents. Scanning electron microscopy was used to prove the occurrence of thermoplasticization of the esterified fibers. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 575–586, 2000

**Key words:** bagasse; esterification; succinic anhydride; thermoplasticization; esterified bagasse composites; dimensional stability; mechanical properties

## INTRODUCTION

In part I of this work,<sup>1</sup> bagasse fiber was esterified using succinic anhydride (SA), in absence of solvent, with the aim of modify mainly the thermoplastic matrix of bagasse, that is, to modify mainly hemicelluloses and lignin, and to keep cellulose as a reinforcing element. Although dynamic mechanical thermal analysis (DMTA) results showed that  $\tan \delta$  peak temperature of esterified bagasse was lower than that of untreated bagasse, thermogravimetric analysis (TGA) results showed considerable weight loss in the same  $\tan \delta$  peak temperature range. In the present work, composites were prepared from esterified fiber having different total ester and monoester and diester contents by hot-pressing without ad-

hesive. Dimensional stability and mechanical properties (bending strength, tensile strength, hardness, and impact resistance) were studied. Scanning electron microscopy (SEM) was used to investigate the occurrence of thermoplasticity of the esterified fiber matrix.

## EXPERIMENTAL

### Material Preparation, Esterification, and Ester Content Determination

Bagasse (about 2–3 cm long) was hammer milled and screened using a 0.4-mm screen. The fibers were oven dried at 105°C for 6 hours and at 65°C overnight. Esterification of bagasse fibers was performed using the following procedure: The desired percent of succinic anhydride (SA) (based on weight of oven-dried fiber) was dissolved in the least possible amount of acetone, typically, for 1 g of SA, 4–5 ml of acetone was required. The SA

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solution was mixed thoroughly with the fibers to get even distribution of the SA on the fibers. The mixture was left inside a fume hood to allow acetone evaporation and then heated at 100–145°C for 0.25–8 h and 160°C for 0.25–3 h. SA additions from 25% to 200% were used. The fibers were removed from the oven, and excess SA was removed by Soxhlet extraction using acetone for 4 h. Then, the fibers were dried overnight at 65°C and weight gains due to esterification were determined based on the original and final oven-dried fiber weights and reported as weight percent gain (WPG).

For ester content determination, esterified bagasse samples were ground to pass 40-mesh screen and oven-dried at 100°C for 6 h; the ester content of SA-modified fibers was determined as described previously.<sup>2</sup>

#### **Pressing of Esterified Bagasse Fibers into Composites**

Twenty grams of esterified bagasse fiber was pressed using a hydraulic press (Carver Laboratory Press), without adhesive, in a mold 11.43-cm diameter at a temperature of 190, 200, or 210°C for 8 min at a pressure of 92 MPa. The pressed samples had a thickness of about 0.3 cm and a density of 1.36.

#### **Cyclic Thickness Swelling Test of Esterified Bagasse Composites in Water**

Pressed esterified bagasse composites were soaked in water at room temperature. Changes in their thickness were measured every 24 h. The percentage increase in thickness (reversible thickness swelling) was calculated based on the original oven-dry thickness. The samples were then re-oven-dried, and the thickness and swelling (irreversible swelling) were redetermined. The samples were then reimmersed in fresh water, and the thickness and swelling were measured. This cycle was repeated five times. Four replicates of each sample were run, and the results were averaged.

#### **Moisture Sorption of Esterified Bagasse Composites**

Esterified bagasse composite samples were placed in separate rooms at 27°C at 30%, 65%, or 90% relative humidity. Composite samples were weighed at the end of 21 days, and the equilibrium moisture content was determined. Four rep-

licates of each sample were run, and the results were averaged.

#### **SEM Examination of Esterified Bagasse Composites**

Scanning electron micrographs were taken of esterified bagasse fibers and pressed composites using a JOEL 840 scanning electron microscope. All samples were coated with gold. Magnifications of  $\times 50$  and  $\times 400$  were used.

#### **Determination of Sugars Content of Esterified Bagasse Composites**

Esterified bagasse composites were ground using 40-mesh sieve, immersed in distilled water and stirred at room temperature for 2 h, and left overnight, filtered, and washed thoroughly with water, and oven-dried at 65°C under vacuum overnight before analysis. Sugars content of bagasse was determined using an HPLC technique according to the method of Pettersen and Schwandt.<sup>3</sup>

#### **Fourier Transform Infrared of Esterified Bagasse Composites**

The esterified bagasse composites were ground to pass 40-mesh sieve, immersed in distilled water and stirred for 2 h, and left overnight, washed thoroughly with water, oven-dried at 105°C for 6 h, and kept in a desiccator. Fourier transform infrared (FTIR) spectroscopy was performed using a Nicolet 6000 spectrophotometer. Samples of each modification were ground to pass 100-mesh screen, oven-dried at 105°C for 6 h, mixed with KBr in a ratio of 1 : 200 mg (bagasse : KBr), and pressed under vacuum to form pellets. Absorbance was measured over a range from 4000 to 400  $\text{cm}^{-1}$ . For measuring the intensity at specific wave number, two specimens of each sample were tested, and the results were averaged.

#### **Ester Content Determination of Esterified Bagasse Composites**

Determination of monoester and diester contents of esterified bagasse composites was carried out as mentioned before except that sample preparation was as follows.

To study the effect of pressing conditions on the ester content, half of the composite was ground to pass a 40-mesh sieve, immersed in distilled water and stirred at room temperature for 2 h, soaked overnight, filtered and washed thoroughly with

**Table I DMTA Results of Esterified Bagasse Fibers**

Total Ester Content (%)	Preparation Conditions	Tan $\delta$ Peak Temperature (°C)
Untreated bagasse	None	252
6.2 (M, 5.0; D, 1.2)	145°C, 0.25 h	225
8.6 (M, 7.1; D, 1.5)	130°C, 1 h	221
13.9 (M, 11.7; D, 2.2)	160°C, 1 h	219
19.2 (M, 17.0; D, 2.2)	130°C, 1 h	214
27.5 (M, 26.5; D, 1.0)	100°C, 3 h	205
32.4 (M, 21.3; D, 11.1)	160°C, 1 h	197
35.3 (M, 32.7; D, 2.6)	130°C, 2 h	199
42.5 (M, 24.7; D, 17.8)	145°C, 5 h	197

M, monoester content (%); D, diester content (%).

distilled water, and oven-dried at 105°C overnight and ester determination was carried out. The other half of the composite was ground to pass 40-mesh sieve, and ester determination was carried out directly without washing.

#### Mechanical Properties Testing of Esterified Bagasse Composites

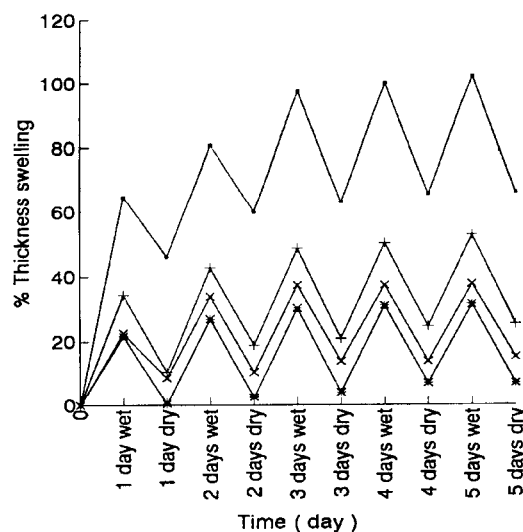
For esterified bagasse composites, the following ASTM methods were used: ASTM D 638-90 was used for tensile properties testing,<sup>4</sup> ASTM D 785-89 was used for hardness testing,<sup>5</sup> ASTM D 256-90b was used for impact resistance testing,<sup>6</sup> and ASTM D 790-90 was used for flexural properties testing.<sup>7</sup> For flexural properties testing, a three-point loading system was used, and the span to depth ratio was 16 to 1.

## RESULTS AND DISCUSSION

#### Properties of Composites Made From Esterified Bagasse Fibers

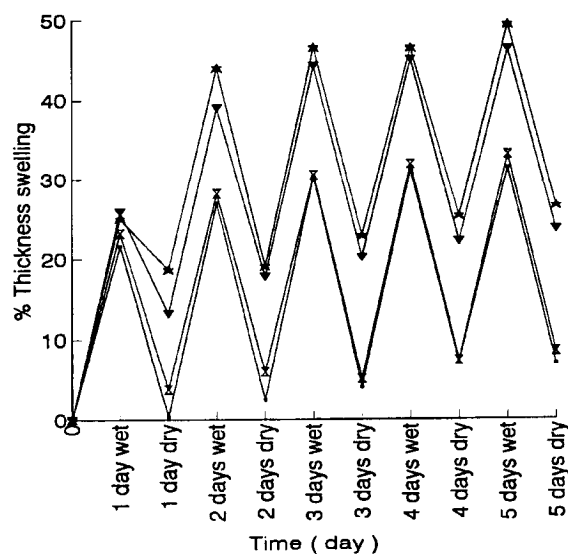
##### Dimensional Stability

In part I of this work,<sup>1</sup> it was found from DMTA results that esterified bagasse fibers had tan  $\delta$  peak temperature range from 197 to 225°C depending on the total ester content (Table I). However, as seen from TGA and DSC results, decarboxylation of esterified bagasse fibers was started at about 181–189°C, depending on the ester content of the fibers. Initial weight loss of the untreated bagasse fibers was found at 233°C. So, the purpose of this study was to determine the



**Figure 1** Effect of total ester content on thickness swelling of esterified bagasse composites. Pressing conditions: 190°C, 8 min. (■), Total ester 13.8%; (+), total ester 19.1%; (\*), total ester 35.3%; (x), total ester 27.6%.

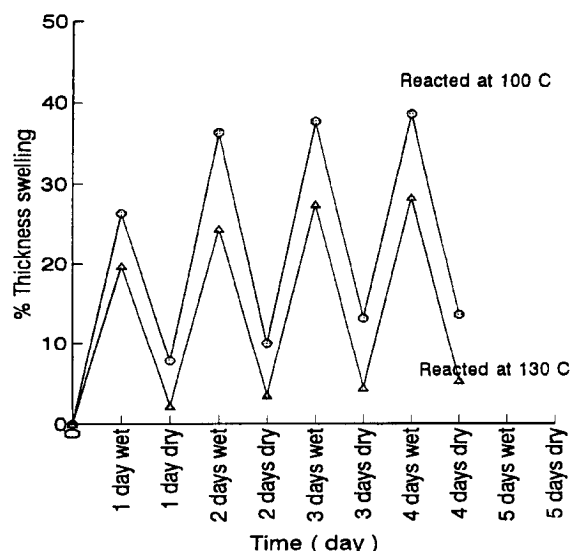
most suitable pressing conditions to prepare composites with the best dimensional stability and least possible degradation. Esterified bagasse fiber samples with different total ester, monoester,



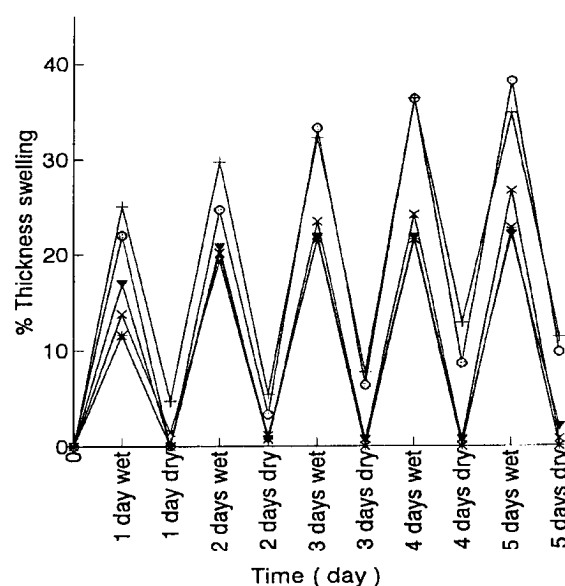
**Figure 2** Effect of monoester and diester contents on thickness swelling of esterified bagasse composites. M, % monoester content; D, % diester content. Pressing conditions: 190°C, 8 min. (■), M 32.7 & D 2.6; (◆), M 26.7 & D 6.9; (▼), M 21.8 & D 13.7; (\*), M 29.1 & D 14.6.

and diester contents were chosen and pressed into composites at 190–210°C for 8 min. The cyclic thickness swelling test in water was used to evaluate dimensional stability of pressed esterified bagasse composites.

Figures 1 and 2 show the results of cyclic water thickness swelling tests for 5 days of the esterified bagasse composites pressed at 190°C for 8 min. The composite made from untreated bagasse fibers fell apart after 30 min of water soaking, while even esterified bagasse composite of low ester content (total ester 13.8%) did not fall apart despite of its high reversible and irreversible swelling. As shown in Figure 1, increasing the total ester content resulted in a decrease in both of the reversible and irreversible thickness swelling. Composites that had a total ester content lower than 20% had high reversible and irreversible thickness swelling, while samples having higher total ester content had lower reversible and irreversible thickness swelling. These results are in agreement with the DMTA results (Table I), which indicated that esterified bagasse fiber samples that had a total ester content less than about 20% had a  $\tan \delta$  peak temperature at about 225°C that is, significantly higher than the pressing temperature used, while esterified bagasse fiber samples that had a higher total ester content than about 20% had a  $\tan \delta$  peak temperature of 197–205°C. Figure 2 shows thickness swelling of

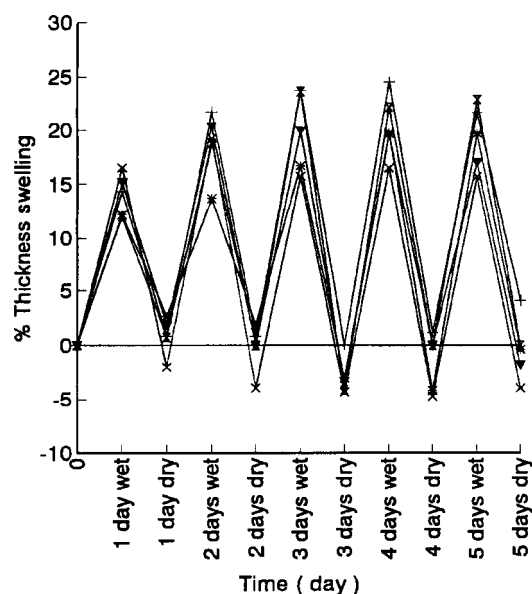


**Figure 3** Effect of reaction temperature on thickness swelling of esterified bagasse composites. M, % monoester content; D, % diester content. Pressing conditions: 190°C, 8 min. ( $\Delta$ ), M 26.7 & D 2.5; ( $\circ$ ), M 26.5 & D 1.0.



**Figure 4** Effect of monoester and diester contents on thickness swelling of esterified bagasse composites. M, % monoester content; D, % diester content. Pressing conditions: 200°C, 8 min. (+), M 13.6 & D 0.2; (\*), M 32.7 & D 2.6; (x), M 27.3 & D 6.7; ( $\circ$ ), M 18.4 & D 3.2; ( $\blacktriangledown$ ), M 21.8 & D 11.1.

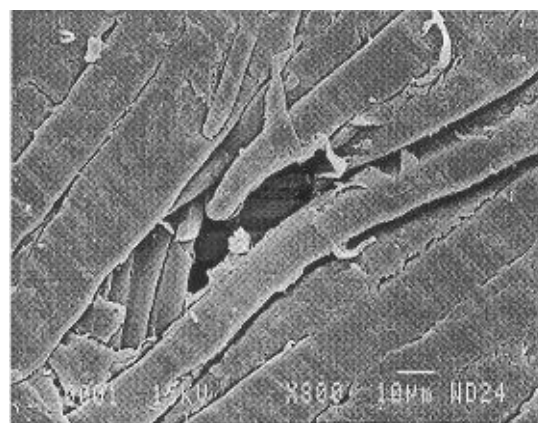
esterified bagasse composite samples having different diester contents. As the diester content increased, the reversible and irreversible thickness swelling increased. This may mean that composites that had high diester content did not flow enough during pressing to the degree at which the stress resulted during pressing could be released. This agrees with the previous findings of Hon and Xing<sup>8</sup> and Matsuda and Ueda,<sup>9</sup> who found that the higher the diester content of carboxylic acid anhydrides-esterified wood, the lower the flow properties and moldability. The composite that had the highest monoester content and the lowest diester content (monoester content 32.7% and diester content 2.6%) had the lowest reversible and irreversible thickness swelling. Figure 3 shows cyclic thickness swelling of two esterified bagasse composites with nearly the same ester content, but the esterified fibers of one of them were prepared by reacting SA with bagasse fibers at 100°C (below melting point of the anhydride), and the fibers of the other one were prepared at 130°C (above its melting point). The composite for which the fibers were prepared at 130°C had better dimensional stability than that for which the fibers were prepared at 100°C. This is expected since reacting the fibers with SA in its solid state would lead to only reaction at the surface of fibers, while



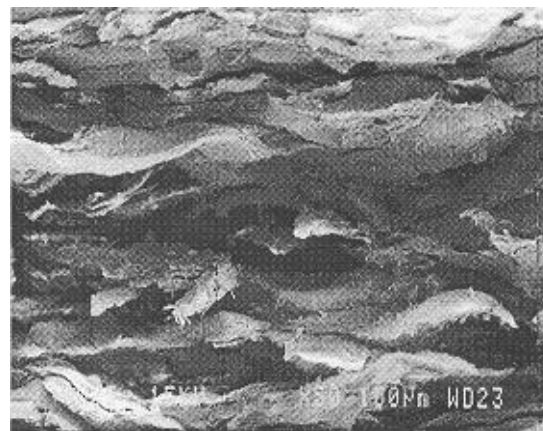
**Figure 5** Effect of monoester and diester contents on thickness swelling of esterified bagasse composites. M, % monoester content; D, % diester content. Pressing conditions: 210°C, 8 min. (+), M 13.6 & D 0.2; (\*), M 32.7 & D 2.6; (x), M 27.3 & D 6.7; ( $\bar{x}$ ), M 26.5 & D 1.0; ( $\blacktriangledown$ ), M 21.8 & D 11.1.

in its liquid state, SA would be able to penetrate the cell wall of the fibers.

Figure 4 shows the cyclic thickness swelling of esterified bagasse composites pressed at 200°C for 8 min. It is clear that composites that had total ester contents of 21.6% or below showed poor dimensional stability. Composites that had total ester content greater than 33% showed the best dimensional stability; irreversible thickness swelling values from 0.0% to 1.5% were found for these composites. This probably indicates that the softening temperature of these composites had been reached during pressing at 200°C, and com-



(a)



(b)

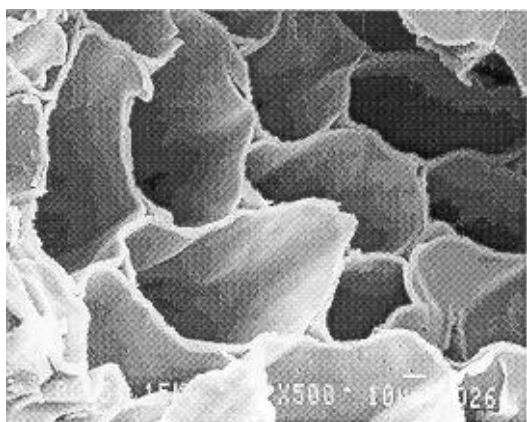
**Figure 6** SEMs of untreated bagasse composite pressed at 190°C for 8 min. (a) Surface; (b) cross section.

plete flow of the thermoplastic portion of the matrix took place. Increasing the diester content resulted in an increase in the initial reversible

**Table II** Equilibrium Moisture Content of Esterified Bagasse Composites

Total Ester Content (%)	EMC at 30% RH			EMC at 65% RH			EMC at 90% RH		
	190°C, 8 min	200°C, 8 min	210°C, 8 min	190°C, 8 min	200°C, 8 min	210°C, 8 min	190°C, 8 min	200°C, 8 min	210°C, 8 min
Untreated bagasse	2.6	2.8	2.8	7.0	6.1	6.0	18.0	17.6	17.1
14.8 (M, 13.6; D, 0.2)	2.5	2.6	2.6	6.6	5.9	5.7	17.2	17.2	15.6
21.6 (M, 18.4; D, 3.2)	2.5	2.8	2.6	4.4	5.8	5.8	13.1	14.2	13.4
35.3 (M, 32.7; D, 2.6)	1.4	1.7	1.8	4.3	5.3	4.5	12.9	13.2	12.9
33.8 (M, 27.3; D, 6.5)	1.8	2.0	2.0	5.3	5.1	4.8	12.6	12.3	13.9
33.9 (M, 21.8; D, 11.1)	1.8	1.4	1.5	4.1	4.7	4.1	13.1	13.6	12.6

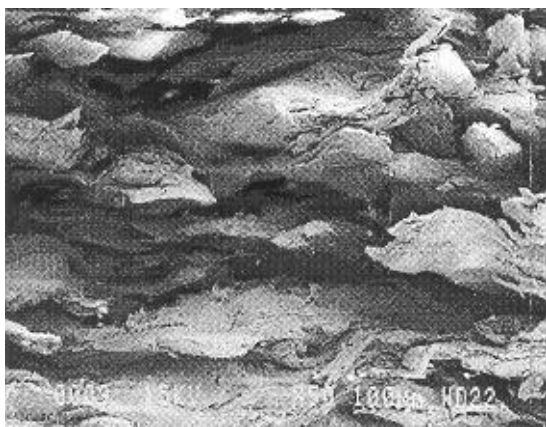
M, monoester content (%); D, diester content (%).



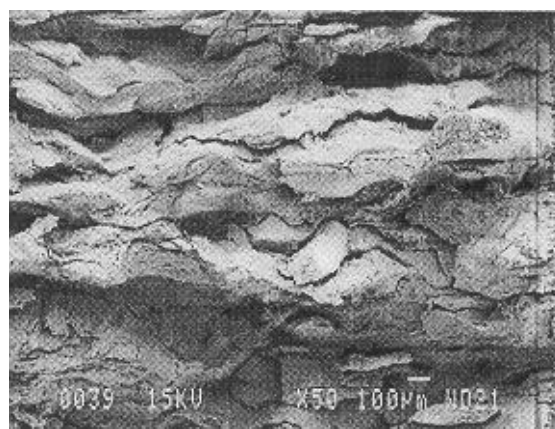
**Figure 7** SEM of an esterified bagasse fiber sample before pressing. Ester content 32.3%.

thickness swelling, that is, higher rate of swelling.

Figure 5 shows the cyclic thickness swelling of composites pressed at 210°C for 8 min. These composites had lower thickness swelling than when they were pressed at 200°C for 8 min. The relation between monoester and diester content and the thickness swelling was similar to that found in case of composites pressed at 200°C for 8 min, but negative irreversible thickness swelling was found in case of composites that had total ester content greater than 33% and pressed at 210°C for 8 min. This may be due to degradation of these composites during pressing and subsequent leaching of degradation products during the test. The effect of pressing conditions on the chemical compositions of the composites will be discussed later.



**Figure 8** SEM of an esterified bagasse composite pressed at 190°C for 8 min. Ester content 13.8%.



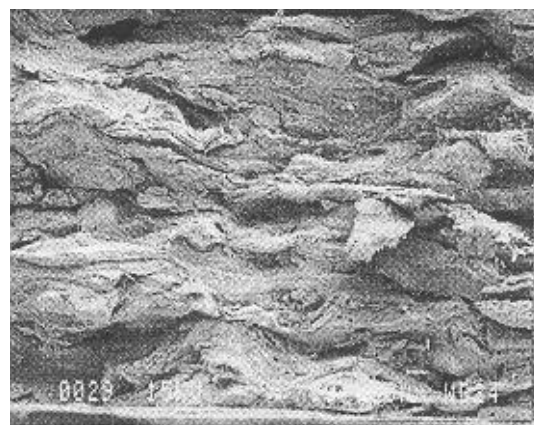
**Figure 9** SEM of an esterified bagasse composite pressed at 210°C for 8 min. Ester content 13.8%.

#### *Equilibrium Moisture Content of Esterified Bagasse Composites*

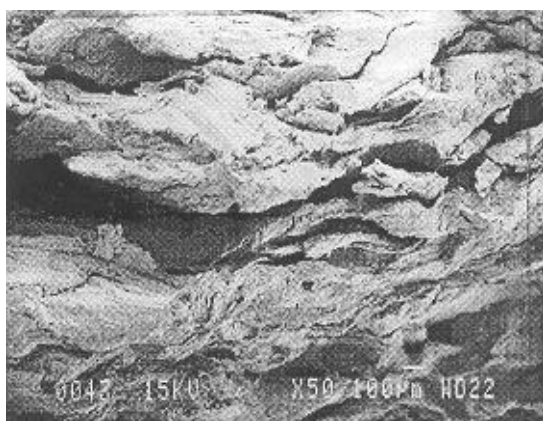
Table II shows the equilibrium moisture content (EMC) of different esterified bagasse composites pressed at 190, 200, and 210°C for 8 min. From the table it is clear that, at each of the relative humidities used, changing pressing temperature from 190 to 210°C had no significant effect on EMC of the different composites. At 30% relative humidity, the composite that had monoester 13.6% and diester content 0.2% had an EMC similar to that of untreated bagasse composites. Composites that had a higher ester content (about 33%) had lower EMC.

#### *SEM of Esterified Bagasse Composites*

Figure 6 shows SEMs of the face and cross section of untreated bagasse composite. The untreated



**Figure 10** SEM of an esterified bagasse composite pressed at 190°C for 8 min. Ester content 35.3%.



(a)



(b)

**Figure 11** SEMs of an esterified bagasse composite. Ester content 35.3%. (a) Pressed at 200°C for 8 min; (b) pressed at 210°C for 8 min.

fibers have a limited tendency to thermally flow under heat and pressure, and the fibers are still separated from each others after pressing. The cross section shows large voids and loose packing of the fibers.

Figure 7 shows the SEM of an esterified fiber sample before pressing (monoester content 21.1% and diester content 11.2%); the cell wall still looks normal, and no rupture or splitting was observed as a result of esterification. This may be an evidence of modifying only the amorphous matrix and may be the assessible cellulose but not the crystalline cellulose. Modifying crystalline cellulose usually results in swelling of cell walls, and at high weight gain, rupture of cell walls may occur.<sup>10,11</sup> It was found in part I that the crystal-

linity index of esterified-bagasse fibers did not decrease as the ester content of fibers increased.<sup>1</sup>

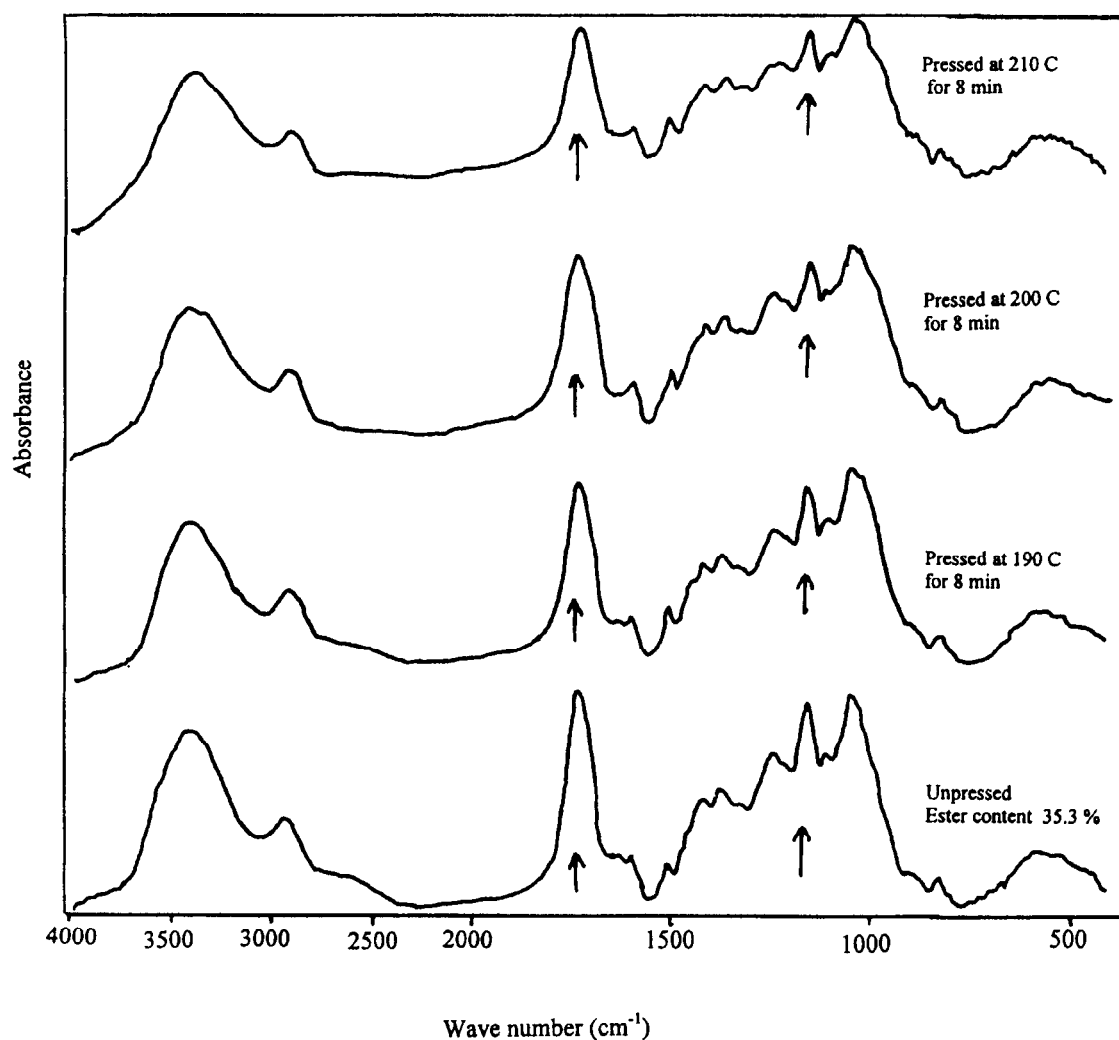
Figure 8 shows the cross section of an esterified bagasse composite with a total ester content of 13.8% (monoester 13.6% and diester 0.2%) and pressed at 190°C for 8 min. These fibers show some thermal flow as compared to the untreated bagasse composite, but little thermoplasticity was achieved under this pressing condition. Pressing the same composites at 210°C for 8 min resulted in a more compact cross section as shown in Figure 9. Figure 10 shows an SEM of cross section of an esterified bagasse composite with a total ester content of 35.3% (monoester 32.7% and diester 2.6%) and pressed at 190°C for 8 min. The cross section is very compact, and the fibers show adhesion to each other. The flow of the thermoplastic portion is clear because no separate fibers are apparent. Similar SEMs were obtained for the same composite but pressed at 200 and 210°C for 8 min (Fig. 11); similar SEMs were obtained for the other esterified bagasse composites that had a total ester content greater than 33% and pressed at the same pressing conditions (Fig. 12).

#### Effect of Pressing Conditions on Chemical Structure and Thermoplastic Properties of Esterified Bagasse Composites

There is a possibility of chemical degradation of bagasse during the pressing step. If the softening of the esterified bagasse fibers found in the preceding sections is chiefly caused by degradation, the phenomenon of softening the bagasse matrix will be of little significance. Therefore, the occur-



**Figure 12** SEM of an esterified bagasse composite pressed at 190°C for 8 min. Ester content 42.5%.



**Figure 13** IR spectra of esterified bagasse fiber sample before and after pressing it into composite at 190, 200, or 210°C for 8 min. Total ester content 35.3%.

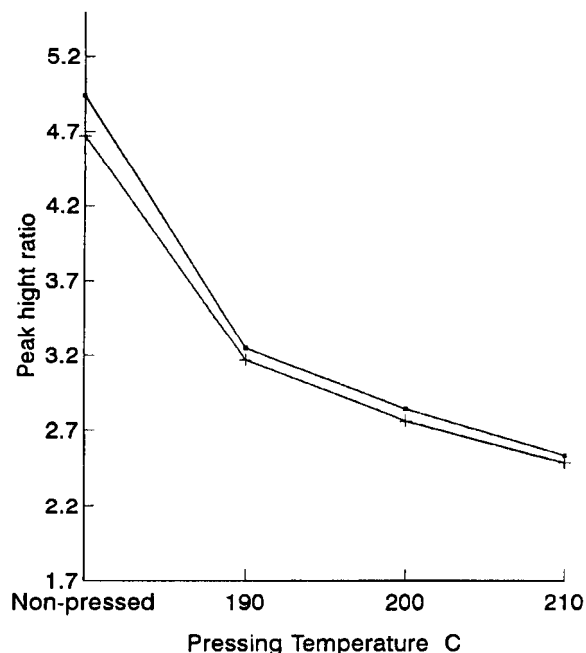
rence of degradation during pressing has been examined briefly using FTIR spectroscopy, HPLC for sugars analysis, and ester content determination.

#### *Effect of Pressing Conditions on FTIR of Esterified Bagasse Fibers*

Figure 13 shows the IR spectra of an esterified bagasse fiber sample before and after pressing it into composites at 190, 200, and 210°C for 8 min. As shown, there is no meaningful changes in major peaks at about 3400  $\text{cm}^{-1}$  (O—H stretching), 2900  $\text{cm}^{-1}$  (C—H stretching of methylene and methyl groups), 1735  $\text{cm}^{-1}$  (C=O ester stretching), 1160  $\text{cm}^{-1}$  (C—O ester stretching), and 1050

$\text{cm}^{-1}$  (C—O stretching of primary and secondary alcohol). However, following the intensities of the peaks at 1735  $\text{cm}^{-1}$  (C=O ester stretching) and at 1160  $\text{cm}^{-1}$  (C—O ester stretching) of the esterified fibers before and after pressing shows a decrease in intensities of these peaks due to pressing. The C=O and C—O band intensities were represented by the ratio of the peak height of these peaks to the peak height of the peak at 1514  $\text{cm}^{-1}$ , which is assigned to aromatic ring stretching. Figure 14 shows this decrease in the intensity as a result of increasing the pressing temperature. This may be due to de-carboxylation of the esterified fibers during pressing, as concluded from the TGA results.





**Figure 14** Effect of pressing temperature on the intensity of C=O and C—O bands in the FTIR spectra of an esterified bagasse composite. Monoester content 32.7% & diester content 2.6%. Pressing time: 8 min. (■), C=O band; (+), C—O ester band.

#### *Effect of Pressing Conditions on the Ester Content of Esterified Bagasse Fibers*

As mentioned in the last section, IR spectra of hot-pressed esterified bagasse composites were essentially the same as those of esterified bagasse fibers before pressing, but the intensities of some of the major peaks were reduced as a result of pressing the fibers. These changes indicate that some de-carboxylation and/or de-esterification occurred. Table III shows the saponification value and the acid value of an esterified bagasse fiber sample before and after pressing at 190, 200, and 210°C for 8 min. From the results of nonleached composites (composites that were ground and not

leached with water), there was an increase in both the acid value and the saponification value due to pressing. The increase in acid value due to pressing may be due to de-esterification during pressing and formation of succinic acid. There was negligible change in both the acid value and the saponification value as the pressing temperature increased from 190 to 210°C. On the other hand, in case of composites that were leached with water before ester determination, there was a decrease in the acid value as a result of pressing. This decrease did not significantly change because of higher pressing temperatures. The decrease in acid value may indicate not only de-esterification or de-carboxylation reactions but also di-esterification reaction as well. The results are in agreement with the findings of Matsuda and Ueda,<sup>12</sup> who found that ester bonds of SA-esterified wood meal were comparatively stable during hot-pressing at 160°C but hot-pressing at 180°C for 10 min caused de-esterification and di-esterification of the esterified fibers.

#### *Effect of Pressing Conditions on the Hemicellulose Component of Esterified Bagasse Fibers*

To determine the effect of pressing conditions on carbohydrate components of bagasse, that is, cellulose and hemicelluloses, sugars analysis of hemicellulose and cellulose components was carried out on an esterified sample before and after pressing. The results are reported in Table IV. Pressing esterified bagasse fibers into composites at 190–200°C had no effect on glucan and xylan contents, whereas pressing the esterified bagasse fibers into composites at 210°C caused a slight decrease in xylan and arabinan content. This means that slight hemicelluloses degradation happened during pressing the esterified fibers at 210°C. This may explain the shrinkage of esterified bagasse composites pressed at 210°C for 8 min during thickness swelling test in water as discussed earlier. Chow et al.<sup>13</sup> concluded from

**Table III** Constituent Sugars Analysis of Hemicellulose and Cellulose of an Esterified Bagasse Composite Sample

Pressing Conditions	% Arabinose	% Galactose	% Glucose	% Xylose	% Mannose
Nonpressed	1.54	0.36	34.47	19.50	0.07
190°C, 8 min	1.54	0.39	34.39	19.45	0.16
200°C, 8 min	1.55	0.44	33.98	19.41	0.11
210°C, 8 min	1.15	0.38	36.17	17.70	0.08

Total ester of the sample 19.1% (monoester 17.0% and diester 2.1%)

**Table IV Effect of Pressing Conditions on AV and SV on an Esterified Bagasse Fiber Sample**

	Non-leached		Leached	
	AV	SV	AV	SV
Nonpressed esterified fibers	1.77	6.47	1.60	5.92
Pressed at 190°C, 8 min	2.44	6.82	1.40	5.89
Pressed at 200°C, 8 min	2.47	6.69	1.43	6.01
Pressed at 210°C, 8 min	2.56	6.80	1.43	6.12

AV, acid value; SV, saponification value. Monoester content 32.7 and diester content 2.6.

the results of IR, X-ray, and DTA that heating oven-dried wood exhibited neither physical nor chemical change at less than 200°C.

#### Physical and Mechanical Properties of Highly Esterified Bagasse Composites

Within our experimental conditions, it was found that the esterified bagasse fiber composite that had the highest monoester (32.7%) and lowest diester (2.6%) contents gave the highest dimensional stability when pressed at 200°C for 8 min. The DMTA results of esterified bagasse fibers showed that this sample had relatively low  $\tan \delta$  peak temperature (199°C). This sample was used in this section to study the mechanical properties of the produced composites. The mechanical properties of those composites are shown in Table V. The maximum strength values were obtained by pressing the esterified fibers at 200°C for 8 min; increasing the pressing temperature to 210°C caused a decrease in strength properties, especially the tensile strength. All these composites

had a very smooth and hard surface, as seen from the Rockwell hardness results in the same table. It is interesting to note the relatively high strength properties of composites made from esterified bagasse fibers pressed at 200°C for 8 min, without using any added adhesives, compared to the American National Standard (ANSI) of high-density wood particleboard or fiberboard. The esterification enhanced the bagasse fibers self-adhesion property because of plasticization of the bagasse matrix during pressing. The ANSI requirements for high-density wood particleboard are 2.76 GPa for modulus of elasticity (MOE) and 23.44 MPa for modulus of rupture (MOR). The esterified bagasse composite (pressed at 200°C for 8 min) had MOE 8.41 GPa and MOR of 51.08 MPa. Yamawaki et al.<sup>14</sup> prepared thermally autoadhered, medium-density fiberboard from cyanoethylated wood fibers (the density of boards was 0.75 g/cm<sup>3</sup>). The maximum MOR and MOE of the prepared boards obtained were 37.2 MPa and 2.4 GPa, respectively, by pressing the cyanoethylated wood fibers at 240°C for 10 min. The MOR

**Table V Mechanical Properties of Esterified Bagasse Composites**

	Pressing Conditions		
	190°C, 8 min	200°C, 8 min	210°C, 8 min
Density (g/cm <sup>3</sup> )	1.36	1.36	1.36
Modulus of rupture (MPa)	44.98 (3.21)	51.08 (2.06)	43.26 (3.37)
Modulus of elasticity (GPa)	7.98 (0.49)	8.41 (0.55)	7.55 (0.55)
Tensile modulus (GPa)	20.51 (3.6)	21.4 (3.6)	11.4 (1.1)
Tensile strength (MPa)	6.02 (1.3)	6.6 (0.5)	3.2 (0.3)
Notched Izod impact (J/m)	26.35 (0.2)	28.54 (0.24)	20.00 (0.17)
Rockwell hardness <sup>a</sup>	79.56 (2.26)	82.50 (2.38)	78.43 (1.26)

The composites had a total ester content of 35.3% (monoester 32.7% and diester 2.6%). Values in parentheses are the standard deviation.

<sup>a</sup> Scale E was used in the test.

**Table VI Comparison between the Properties of Conventional Bagasse-Phenol Formaldehyde (PF) Fiberboard and Esterified Bagasse Composite Samples**

	Bagasse-PF Fiberboard <sup>a</sup>	Esterified Bagasse Composites <sup>b</sup>
Density (g/cm <sup>3</sup> )	0.64	1.36
Reversible thickness swelling (after 5 cycles)	35.0	22.8
Irreversible thickness swelling (after 5 cycles)	23.0	0.0
Specific modulus of rupture [MPa/(g/cm <sup>3</sup> )]	21.7	37.65
Specific modulus of elasticity [GPa/(g/cm <sup>3</sup> )]	2.20	6.18
Specific tensile modulus [GPa/(g/cm <sup>3</sup> )]	—	15.54
Specific tensile strength [MPa/(g/cm <sup>3</sup> )]	—	4.85
Notched Izod impact (J/m)	—	28.54
Rockwell hardness <sup>c</sup>	—	82.50

<sup>a</sup> Pressing conditions were 180°C for 10 min; 5% phenol formaldehyde resin; tested according to ASTM D 1037. From Rowell and Keany.<sup>15</sup>

<sup>b</sup> The esterified bagasse composite had total ester content of 35.3% and was pressed at 200°C for 8 min.

<sup>c</sup> Scale E was used in the test.

and MOE were 33 MPa and 2.5 GPa, respectively, when the cyanoethylated fibers were pressed at 200°C for 10 min. It should be noted that the ASTM methods that were used for measuring the strength properties of esterified bagasse composites are different from those usually are used for particleboard and fiberboard concerning sample dimensions and conditioning. Esterified bagasse composites would have different equilibrium moisture content (EMC) from wood particleboard if they are conditioned before testing at the same relative humidity. In addition, the failure mechanism of esterified bagasse composites is different from wood particleboard. Also, if equal cross sections of the prepared esterified bagasse composites and the conventional particleboard are used for mechanical testing, the number of fibers per cross section in testing both of them will be different. Table VI shows a comparison between the properties of bagasse fiberboard made from untreated bagasse fibers using 5% phenol formaldehyde resin<sup>15</sup> and esterified bagasse composite made from esterified bagasse fibers without adhesive. The esterified bagasse composite had lower reversible thickness swelling than the conventional bagasse fiberboard and, more important, had no irreversible thickness swelling, while the conventional bagasse fiberboard had irreversible thickness swelling of 22.8%. It should be taken in consideration that the density of the conventional bagasse fiberboard was 0.64 g/cm<sup>3</sup>, while that of the prepared esterified bagasse composite was 1.36 g/cm<sup>3</sup>. Generally, increasing the density of conventional types of board causes an increase in reversible and irreversible thickness swelling due to

the increased mass and the high pressure applied to produce high-density board. The esterified bagasse composite had an MOE more than twice that of bagasse fiberboard, and the MOR was much higher than that of bagasse fiberboard.

#### *Effect of Monoester and Diester Contents on the Mechanical Properties of Esterified Bagasse Composites*

Table VII shows the mechanical properties of esterified bagasse composites having different monoester and diester contents. All composites were pressed at 200°C for 8 min. Increasing the diester content of the composites resulted in a decrease in MOR, MOE, and Rockwell hardness. No significant effect of increasing the diester content on the tensile strength and the impact resistance was found. The decrease in the MOE, the MOR, and the hardness of the composites as a result of increasing the diester content may be due to the lesser thermoplasticity of the esterified matrix of bagasse in case of the composites that had higher diester content. Better flow of the esterified matrix of bagasse may result in better adhesion between the fibers during pressing. Crosslinking of the esterified bagasse matrix, as a result of diester formation, did not result in an increase of mechanical properties of the esterified bagasse composites, especially the MOE. This may be because the crosslinking that occurred is of intramolecular type and not intermolecular. In other words, crosslinking during esterification took place within the fiber, and little crosslinking, if any, took place between different fibers during pressing.

**Table VII Effect of Monoester and Diester Content on Mechanical Properties of Esterified Bagasse Composites**

	Monoester Content (M) and Diester Content (D)		
	M 32.7% and D 2.6%	M 27.6% and D 6.3%	M 21.11% and D 11.1%
Density (g/cm <sup>3</sup> )	1.36	1.36	1.36
Modulus of rupture (MPa)	51.08 (2.06)	45.82 (3.60)	42.60 (5.69)
Modulus of elasticity (GPa)	8.41 (0.55)	6.27 (0.53)	6.48 (0.83)
Tensile modulus (GPa)	21.4 (3.6)	22.1 (1.97)	22.8 (3.04)
Tensile strength (MPa)	6.6 (0.5)	8.4 (0.5)	6.0 (0.4)
Notched Izod impact (J/m)	28.54 (0.24)	26.33 (0.36)	27.06 (0.38)
Rockwell hardness <sup>a</sup>	82.50 (2.38)	69.12 (2.65)	57.23 (2.47)

Values in parentheses are the standard deviation.

<sup>a</sup> Scale E was used in the test.

Hon and Xing<sup>8</sup> and Matsuda and Ueda<sup>9</sup> found that the higher the diester content of SA-modified wood the lower the flow properties and moldability.

density wood particleboard and also having much better dimensional stability.

## CONCLUSIONS

From the research conducted in this investigation, the following could be concluded.

1. in part I of this work, thermoplastization of bagasse by esterification was not clearly proved, because although DMTA results showed that tan  $\delta$  peak temperature of esterified bagasse was lower than that of untreated bagasse, the TGA results showed considerable weight loss in the same tan  $\delta$  peak temperature range. The occurrence of thermoplasticization of the esterified bagasse fibers was proved using SEM and is supported by the absence of reversible swelling of some esterified bagasse composites.
2. On studying the effect of pressing conditions used on the esterified fibers using FTIR, ester determination, and hemicellulose sugar analysis, it could be concluded that de-esterification occurred on pressing the fibers at 190–210°C for 8 min. Also, hemicellulose degradation occurred on pressing the esterified fibers at greater than 200°C.
3. The mechanical properties of a selected composite showed that it is possible to obtain a nonconventional composite having mechanical properties significantly higher the ANSI standards required for conventional high-

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